D14

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C08F 8/00

A1

(11) International Publication Number: WO 98/02468

(43) International Publication Date: 22 January 1998 (22.01.98)

(21) International Application Number: PCT/GB97/01876

(22) International Filing Date: 11 July 1997 (11.07.97)

(30) Priority Data:
9615025.5 17 July 1996 (17.07.96) GB

(71) Applicant (*for all designated States except US*): BP CHEMICALS (ADDITIVES) LIMITED [GB/GB]; BP House, Breakspear Way, Hemel Hempstead, Hertfordshire HP2 4UL (GB).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*): MORETON, David, John [GB/GB]; 76 Ellesmere Avenue, Off Holderness Road, Hull, East Yorkshire HU8 9BT (GB).

(74) Agent: SMITH, Julian, Philip, Howard; BP International Limited, Group Patents & Agreements, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PRODUCTION OF SUBSTITUTED POLYISOBUTENES

(57) Abstract

A process is disclosed for producing a functionalised polyisobutene (PIB) derivative, which comprises reacting a PIB with hydrogen bromide, and then reacting the resultant PIB bromide so as to displace at least one bromine atom with another functional group. Very low levels of residual halogen in the final product are achieved using this process compared with known chlorination processes, particularly if the PIB has a high percentage of vinylidene C=C bonds

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

PRODUCTION OF SUBSTITUTED POLYISOBUTENES

The present invention relates to polyisobutenes, and in particular to hydrohalogenated and aminated polyisobutene derivatives and processes for making them, and hydrocarbon fuel compositions containing them.

Hydrocarbon fuels generally contain numerous deposit-forming substances. When such fuels are used in internal combustion engines, deposits tend to form on and around constricted areas of the engine in contact with the fuel. For example in diesel engines, deposits are particularly prevalent in the fuel injection system, which adversely affects the performance of the engine.

It is common practice to incorporate a dispersant/detergent in the fuel to inhibit formation and facilitate removal of such deposits. Particularly efficacious valve inlet port detergents are those based on polyisobutene (PIB) amines. For example PIB succinimides are well-known as lubricating oil detergents, although they have been known for use in fuels.

Commercial PIBs are today of two types. So-called "low-reactive" PIBs consist of largely of saturated chains or chains in which the unsaturation is non-terminal. An example is the product HYVIS®, available from BP Chemicals Limited, in which 96% of the unsaturation is non-terminal. Recently a new type of "high-reactive" PIB has become available, in which a majority (about 80%) of the terminal olefinic double bonds are of the vinylidene type: $-CH_2-C(CH_3)=CH_2$. Examples are ULTRAVIS®, also available from BP Chemicals Limited, and GLISSOPAL, available from BASF. As their name suggests these PIBs are more reactive than conventional PIBs because of the high proportion of terminal vinylidene bonds. Preferred PIBs for use in making amine derivatives have a molecular weight in the range from 750 to 1500, with up to 40% by weight of a

PIB having a molecular weight greater than 1500, for example up to 5000, typically about 2400.

In a leading commercial process, PIB amines are made by chlorinating the PIB, and then aminating the resultant PIB chloride. This suffers from the disadvantage that there is always a small but significant amount of residual chlorine (from about 0.5 to as much as 3 wt%) left in the final product, which has the potential to produce traces of toxic dioxins (cyclic hydrocarbons containing oxygen and chlorine) upon combustion of fuel containing the PIB amine as additive. Chlorine is now regarded as undesirable in many products. As a result there is a need to reduce substantially or eliminate residual chlorine from PIB amines or other PIB derivatives made via PIB chlorides; the same would apply to bromine if used.

One option to overcome this problem is to avoid the halogenation route altogether. For example EP-A-565285 discloses a process for the production of PIB succinimides which comprises reacting a "high-reactive" PIB with a succinic acylating agent, and then reacting the resultant product with an amine.

However we have discovered that PIB derivatives such as PIB amines can be made by the halogenation route and contain much lower levels of residual halogen than previously known, by using hydrogen bromide rather than Cl_2 to form the PIB halide.

Accordingly in a first aspect the invention provides a process for producing a polyisobutene (PIB) bromide, comprising reacting a PIB with hydrogen bromide. The process for producing PIB derivatives from PIB bromides comprises first forming a PIB bromide in this way, and then reacting the bromide to displace at least one Br with another functional group.

We have found that when such derivatives are made by this route rather than by the known PIB + Cl_2 route, the level of residual halogen after subsequent amination or other functionalisation of the PIB bromide is of the order of ppm instead of %. Thus derivatives of PIB can be made which contain no more than 500 ppm residual bromide, and preferably no more than 100ppm. Levels as low as 50ppm and below can be achieved.

Preferred derivatives of PIB bromides include polyisobutene amines, succinic anhydrides, succinimides, succinic acids and the esters of succinic acids, including any compounds which can function as carboxylic acylating agents. Such derivatives are well-known in the art.

We have further discovered that if the PIB is specifically a "high reactive" PIB, the level of residual bromine is reduced still further. Moreover, the PIB bromide

in such a case contains a substantial proportion of terminal bromine atoms, which leads to greater reactivity during subsequent functionalisation and obviously to a corresponding level of terminal functional groups, which can have potential advantages in performance of the final product. Accordingly it is preferred that at least 50%, preferably at least 70% of the terminal olefinic double bonds in the PIB are of the vinylidene type. Similarly in preferred functionalised PIB derivatives at least 50%, preferably at least 70% of the functional groups are terminal.

The invention derives from the discovery that the hydrobromination of PIBs appears to differ from that of chlorination in an unexpected way. Addition of Cl_2 to PIBs results in polychlorination, and after further functionalisation many chlorine sites are not functionalised, leading to a high level of residual chlorine. In our experience, hydrochlorination of PIBs is extremely difficult to perform. By contrast hydrobromination occurs readily, and polybromination is virtually eliminated. It is also believed that when a "highly reactive" PIB is hydrobrominated, the hydrobromination occurs in an anti-Markownikov arrangement, i.e. the bromine adds at the less substituted carbon. This is the opposite of what would be expected, and indeed the opposite of what is believed to occur when "low-reactive" PIB is hydrobrominated. This is believed to be responsible for the even lower levels of residual bromine found in functionalised PIBs derived from "high-reactive" PIB, and also to the high proportion of terminal functional groups.

The processes of hydrohalogenation and subsequent nucleophilic substitution are well known, and the invention does not require any special process steps. The process preferably uses hydrogen bromide but may instead use a suitable source of HBr such as an amide salt of HBr which can be made to generate HBr in situ. Solvents for the hydrobromination are not essential but are preferred: alkanes such as hexane or heptane may be used, or acetic acid. The temperature of the reaction may be between -10 and 100°C, but preferably between 10 and 60°C; room temperature is generally adequate. The reaction is generally conducted at atmospheric pressure, but if HBr gas is used this may be supplied under pressure. The reaction is suitably carried out in a vessel resistant to the corrosion effects of HBr, such as a glass-lined or stainless steel vessel.

EXAMPLES

EXAMPLE 1: Hydrobromination of Ultravis 10 ("High-reactive" PIB)

A one litre wideneck flange tap round-bottomed flask fitted with overhead stirrer and paddle with PTFE gland, double surface condenser in reflux mode with

calcium chloride drying tube, pressure equalising dropping funnel (1250ml capacity) and thermocouple/mantle/Eurotherm heating system; was charger with Ultravis 10 (1008.6g, 1 mole) and heptane (400g, solvent). The mixture was stirred until homogeneous and 30% HBr in glacial acetic acid (539g, 2 moles) added at room temperature over 2.5 hours. The temperature increased to 26°C during this time. The mixture was then further heated to 45°C for two hours. 1700g water was then added to quench the reaction, and the mixture left to stand overnight. The mixture was separated into two phases: the upper cloudy phase was siphoned off and washed with 107g heptane in a five litre dropping funnel and the solution neutralised with 240g of a 25% solution w/w of Na_2CO_3 in water. The lower phase was run off and the upper phase transferred to a three litre round-bottomed flask, and the solvent removed by rotary evaporator (100°C, -685mm Hg). The resultant brown liquid was then analysed for bromine content, which was found to be 6.4%.

EXAMPLE 2: Amination of Ultravis 10 hydrobromide

The same apparatus as in 1 above was used, with the exception that the addition funnel was removed, and the condenser set for distillation into a one litre round-bottomed flask. The reaction flask was charged with the Ultravis 10 hydrobromide prepared above (920.1g, 0.85 moles), aminoethylethanolamine (834g, 8.01 moles), and xylenes (105.1g, solvent). The mixture was stirred with a nitrogen sparge and heated to 175°C for three hours, with the condenser in reflux mode. The mixture was then cooled to 110°C, and sodium hydroxide (47% aqueous, 129g, 1.516 moles) added. Stirring was continued for a further two hours. The mixture was then left to stand overnight, following which the condenser was set up for distillation. The reaction was heated to 190°C with stirring at -685mm Hg pressure, and all solvent removed (259g collected). The reactor contents were cooled to 95°C, vacuum released, and 834g of a 3:1 by weight mixture of xylene and 1-butanol added. The mixture was stirred for 30 minutes at 85°C, 378g of water added and then allowed to settle at room temperature overnight.

The mixture was stirred at 80°C for 30 minutes, allowed to settle, and then the clear, dark brown lower aqueous phase siphoned off. This was repeated until the pH of the aqueous phase was 8. The upper pale brown cloudy organic phase removed with 430g of 7% w/w of 1-butanol in water. The solvent was removed from the organic phase on a rotary evaporator at 143°C, -724mm Hg. Crude yield of product was 790.9g. The product was then filtered through a 0.25 inch (6mm) Celite pad to

give 715.7g of a clear golden liquid (76.2% yield). Residual bromine content was found to be less than 50ppm.

EXAMPLE 3: Hydrobromination of Hyvis 10 ("Low-reactive" PIB)

The same apparatus as for Example 1 was used, except that a 1-litre wide neck flange flask was employed. It was charged with Hyvis 10 (253g, 0.253 moles) and heptane (100g, solvent), and the mixture stirred until homogeneous. 30% hydrobromic acid in glacial acetic acid (135g, 0.5 moles) was then added at room temperature over two hours. No exotherm was observed. The reaction was then heated to 45°C and held for two hours, at which point 400ml water was added to quench the reaction followed by more heptane (100ml). The reaction mixture was poured into a 2 litre separating funnel and allowed to settle out. The upper organic phase was retained and washed with 100g of 30% aqueous sodium bicarbonate followed by water (100g), and then dried over magnesium sulphate. The liquid was filtered off via a sinter funnel, and solvent removed on a rotary evaporator at 100°C, -724mm Hg. The yield was 215.3g of a brown, cloudy liquid. Bromine content was determined as 5.5%.

EXAMPLE 4: Amination of Hyvis 10 hydrobromide

The same apparatus as in 1 above was used, with the exception that the addition funnel was removed, and the condenser set for distillation into a 500ml round-bottomed flask. The reaction flask was charged with the Hyvis 10 bromide prepared above (15g, 13.9 mmol), aminoethylethanolamine (13.1g, 125 mmol), and xylenes (105.1g, solvent). The mixture was stirred with a nitrogen sparge and heated to 175°C for three hours, with the condenser in reflux mode. The mixture was then cooled to 110°C, and sodium hydroxide (47% aqueous, 2g, 23.5 mmol) added. Stirring was continued for a further two hours. The mixture was then left to stand overnight, following which the condenser was set up for distillation. The reaction was heated to 190°C with stirring at -685mm Hg pressure, and all solvent removed (259g collected). The reactor contents were cooled to 95°C, vacuum released, and 140g of xylene added. The mixture was stirred for 30 minutes at 85°C, further water added and then allowed to settle at room temperature overnight.

The mixture was stirred at 80°C for 30 minutes, allowed to settle, and then the clear, dark brown lower aqueous phase siphoned off. This was repeated until the pH of the aqueous phase was 8. The upper pale brown cloudy organic phase removed with 5 x 100ml of 7% w/w of 1-butanol in water. The solvent was removed from the

organic phase on a rotary evaporator at 143°C, -724mm Hg. The product was then filtered through a 0.25 inch (6mm) Celite pad to give 6.24g of a clear golden liquid. Residual bromine content was found to be 410ppm.

ENGINE TESTS

The amines prepared in Examples 2 and 4 above were evaluated as detergency additives in fuels according to a standard engine test (M102E), following method CEC F-05 A-93 on a Mercedes Benz M 102.982 engine. The fuel employed was (a) unleaded 95 RON Spanish commercial gasoline for Examples 5/6, and (b) a cleaner CEC fuel for Examples 7/8. The oil was RL-189/1. The amines tested were dosed in the fuel as 17% of a standard additive package which was added at 800ml/m^3 (ppm), giving a dosage rate of the amine itself of 136ppm.

Measurements were made of the inlet valve deposits, and the valves were also given a visual rating. In this test the lower the deposit the better, and the higher the visual rating (out of 10) the better.

EXAMPLE		DEPOSITS (mg)	AVE. VISUAL RATING
5.	Base fuel (a) alone	527	6.64
6.	Base fuel (a) + amine of Ex. 2	57	9.40
7.	Base fuel (b) alone	278	7.59
8.	Base fuel (b) + amine of Ex. 4	42	9.24

These results show that PIB succinimides made according to the process of the invention are very effective at reducing valve deposits in engines.

CLAIMS:

1. Process for producing a polyisobutene (PIB) bromide, comprising reacting a PIB with hydrogen bromide.

2. Process for producing a functionalised PIB derivative, comprising reacting a PIB with hydrogen bromide, and then reacting the resultant PIB bromide so as to displace at least one bromine atom with another functional group.

3. Process according to claim 2 wherein the functionalised PIB derivative is a PIB amine, succinic anhydride or succinimide.

4. Process according to claim 2 or 3 wherein the functionalised PIB derivative has a residual bromine content of 500ppm or less, preferably 100ppm or less and more preferably 50ppm or less.

5. Process according to any preceding claim wherein at least 50% and preferably at least 70% of the functional groups in the functionalised PIB derivative or the bromine atoms in the PIB bromide are terminal.

6. Process according to any preceding claim wherein at least 50% and preferably at least 70% of the terminal olefinic double bonds in the original PIB are of the vinylidene type.

INTERNATIONAL SEARCH REPORT

Intern. ..onal Application No
PCT/GB 97/01876

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F8/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 459 237 A (BASF AG) 4 December 1991 see the whole document ---	1-6
Y	US 3 018 275 A (D. L. COTTLE) 23 January 1962 see column 2, line 43 - line 60; claims 1-5 ---	1-6
Y	US 4 029 592 A (I. PUSKAS) 14 June 1977 see the whole document ---	1-6
A	US 3 786 077 A (R. E. CHANDLER) 15 January 1974 see column 1, line 25 - line 72 see column 2, line 1 - line 20 see column 3, line 7 - line 43; claims 1-5 --- -/--	1

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
17 November 1997	01/12/1997

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Permentier, W

INTERNATIONAL SEARCH REPORT

Inte. .onal Application No
PCT/GB 97/01876

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	FR 1 098 977 A (THE B. F. GOODRICH COMPANY) 29 August 1955 see page 7 - page 8	1
A	EP 0 161 785 A (EXXON RESEARCH AND ENGINEERING COMPANY) 21 November 1985 see claims 1-26	1
A	FR 1 215 641 A (ESSO RESEARCH AND ENGINEERING COMPANY) 20 April 1960 see the whole document	1
A	GB 1 008 656 A (MICHELIN & CIE) 3 November 1965 see claims 1-18	1

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. ...nal Application No
PCT/GB 97/01876

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 459237 A	04-12-91	DE 4017300 A	05-12-91
		DE 59106072 D	31-08-95
		ES 2075265 T	01-10-95
		JP 4227906 A	18-08-92
		US 5122573 A	16-06-92
US 3018275 A	23-01-62	DE 1101762 B	
		FR 1252800 A	10-05-61
		GB 867737 A	
US 4029592 A	14-06-77	US 3960900 A	01-06-76
US 3786077 A	15-01-74	NONE	
FR 1098977 A	29-08-55	NONE	
EP 161785 A	21-11-85	US 4632963 A	30-12-86
		US 4681921 A	21-07-87
		AU 581214 B	16-02-89
		AU 4088385 A	10-10-85
		BR 8501634 A	03-12-85
		CA 1265891 A	13-02-90
		IN 170431 A	28-03-92
		IN 170470 A	28-03-92
		JP 60229905 A	15-11-85
		US 4703091 A	27-10-87
		US 4634741 A	06-01-87
FR 1215641 A	20-04-60	GB 838045 A	
		US 2995545 A	08-08-61
GB 1008656 A		BE 611989 A	
		DE 1150815 B	
		FR 1286688 A	25-07-62
		LU 41011 A	27-02-62
		NL 125556 C	
		NL 273070 A	
		US 3235538 A	15-02-66